Competing Instabilities and the High Field Phases of $(TMTSF)_2ClO_4$

S. K. McKernan,[1] S. T. Hannahs,[2] U. M. Scheven,[1] G. M. Danner,[1] and P. M. Chaikin[1]

[1]*Department of Physics, Princeton University, Princeton, New Jersey 08544*

[2]*Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306*

(Received 10 April 1995)

In this Letter we establish the phase diagram of $(TMTSF)_2ClO_4$ to 30 T and above 0.5 K by transport and magnetization measurements. The high field region is bounded above by a second order transition from metallic to field induced spin density wave state at 5.5 K. Completely contained inside this boundary is a first order line terminating in a critical point. Neither phase boundary shows the large oscillations predicted in recent models. Our results suggest that there are separate transitions on each of the two Fermi surfaces, with only weak coupling between the order parameters.

PACS numbers: 75.30.Fv, 72.15.Gd, 74.70.Kn

The Bechgaard salts, $(TMTSF)_2X$, have served as a remarkable laboratory for the investigation of interacting electrons in low dimensions [1]. They are extremely clean materials with mean free paths of many microns at low temperature. Their simple quasi-one-dimensional band structure with Fermi surfaces consisting of slightly warped parallel sheets belies the complex high field behavior seen experimentally. In this low temperature metallic state of the $X = PF_6$ salt, a moderate field along the **c** (least conducting) direction produces a cascade of transitions to states, exhibiting the quantized Hall resistance $\rho_{xy} \approx h/n2e^2$ in the sequence $n = \ldots 5, 4, 3, 2, 1, 0$ as field is increased. The integer states have been identified as semimetallic (field induced) spin density wave states (or FISDW's) while $n = 0$ is an FISDW insulator. We understand the cascade of FISDW in terms of the "standard model" as originally proposed by Gor'kov and Lebed [2]. The Fermi surface sheets imperfectly nest leaving closed semimetallic pockets. In the presence of a magnetic field the closed orbits are Landau quantized and energy is gained when the Fermi energy lies in a gap. The SDW wave vector adjusts to ensure this condition, but its component along the **a** (most highly conducting) direction is quantized to values $Q_x = 2k_f + n\delta$, where $\delta = ebH/hc$ is the magnetic wave vector appropriate for a field perpendicular to the **a-b** plane and n is the quantum Hall plateau index.

While experiments on the PF_6 salt have been substantially explained by the standard model [3], the ClO_4 salt is different [4]. As in PF_6, we observe the FISDW transitions as $H_{\perp ab}$ is increased. However, the Hall resistances show plateaus but not in the expected order [5]: At a few kelvin, there is reentrance of the metallic phase as field is increased through the FISDW region [6], there is an extremely stable quantum Hall–semimetal phase which persists at 0.5 K from 7.5 to 27 T [7], and there are very strong "fast oscillations" with ($1/H$ behavior) observed throughout the low temperature high field region [8].

In order to explain the differences between these two salts, attention has focused on the anion ordering transition which occurs in ClO_4 at 24 K and dimerizes the system along the **b** direction. The resulting Fermi surface is schematized in Fig. 1. The **b** dimerization leads to two pairs of open orbit Fermi surface sheets. Theoretically, there are several recent explanations or predictions for the high field phase boundary. Some suggest the differences lie in band-structure details or in the competition or coexistence of many order parameters [9]. Other models treat the combined effects of an anion ordering gap, spin density wave gap, and magnetic breakdown [10,11]. The latter tend to yield high field phase boundaries with spectacular oscillations in $1/H$ with periodicity given by the k space area between Fermi surfaces FS1 and FS2. These calculations assume that there is a single transition which causes FISDW's on both FS1 and FS2.

In this Letter we report on a high field phase diagram which is substantially different than anything that has previously been imagined for these systems. On cooling from the metallic state (between 23 and 27 T) there are two transitions at 5.5 and 3.5 K. The "5.5 K" transition is second order while the "3.5 K" transition is part of a first order line that ends at a critical point inside the FISDW phases. Neither transition shows the predicted large oscillations with field. The reentrance of the normal metal at ~4 K with increasing field appears more as a

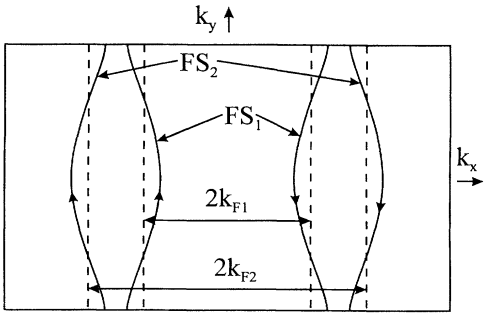

FIG. 1. Schematic of the Fermi surfaces of $(TMTSF)_2ClO_4$, resulting from a dimerization of the system along the **b** axis. Arrows indicate electron orbits in a magnetic field coming out of the page.

 0031-9007/95/75(8)/1630(4)$06.00 © 1995 The American Physical Society

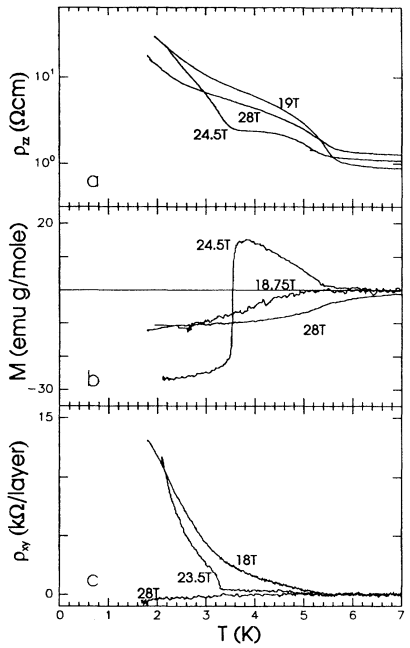

FIG. 2. Fixed field temperature sweeps of ρ_{zz}, ρ_{xy}, and magnetization. Note the second order transition at all fields at ~5.5 K and the first order transition at 3.5 K for 24.5 T (most easily seen in magnetization).

crossover than a transition. The 5.5 K transition, which is essentially independent of field above 15 T, appears to be a metal-metal transition, possibly with an SDW on one FS and a metallic state on the other. The picture which emerges is of distinct transitions on FS1 and FS2. At 5.5 K FS1 goes insulating but produces only induced gaps on FS2. For some range below 5.5 K the induced gaps dominate, but a separate instability on FS2 leads to the first order transition at 3.5 K.

The phase diagram was determined by a combination of five transport measurements ($\rho_{xx}, \rho_{yy}, \rho_{zz}, \rho_{xy}, S_{xx}$, where ρ is resistivity and S is thermopower) and magnetization. Data were collected on three separate runs at the Francis Bitter National Magnet Laboratory and encompassed 11 different samples all of which had been "slow cooled" through the anion ordering transition at 24 K [12]. The measurements directly shown in this Letter are ρ_{xy} and ρ_{zz}, which are particularly sensitive to the transitions, and the magnetization which gives us an idea of the thermodynamics. The Hall resistance ρ_{xy} was obtained using the reciprocity relation, $R_{xy}(H) = R_{yx}(-H)$, to perform subtractions eliminating longitudinal resistance. $R_{xy}(H)$ and $R_{yx}(H)$ were simultaneously measured with two different frequencies (67 and 113 Hz). This allowed real-time computation of the Hall signal, without reversal of field, during the field or temperature sweeps. The magnetization was obtained capacitively and ρ_{zz} conventionally.

In Fig. 2 we show the results of temperature sweeps at three different field regions. On decreasing temperature at 18–19 T we see evidence of a transition in all of the properties at 5.5 K. Below this temperature R_{zz} and Hall resistance increase and the magnetization becomes diamagnetic [13]. These changes indicate a second order transition, which we associate with entering an FISDW. Note that although the resistances rise more rapidly at lower temperatures there is no hint of an additional transition in the 18–19 T data. At ~24 T we observe similar behavior on cooling through 5.5 K, however, the resistances do not increase as much as at 19 T. Moreover, there is a clear transition observed in the resistances at ~3.5 K. The abrupt step in the magnetization at 3.5 K indicates that the transition is first order. Finally, at 28 T we again see evidence of the second order transition at 5.5 K in R_{zz} and magnetization, but the first order transition has vanished. (Field sweeps show that its transition temperature approaches 0 as H goes to 27 T.) The 5.5 K transition is barely visible in Hall resistance at 28 T, suggesting that the carrier density remains high (metallic) through this transition. A similar argument could be made for ρ_{xy} between 5.5 and 3.5 K at 23.5 T. It is interesting to note that ρ_{zz} roughly doubles in the region between the two transitions at 24.5 T, hinting that one of the two FS's is gapped.

In Fig. 3 we show constant temperature field sweeps. Above 5.5 K there is sizable ρ_{zz} magnetoresistance, but there are no observable transitions in any of the measurements. (The metallic state Hall resistance is below our measurement sensitivity.) The data at 4 K reveal a single well-defined transition at ~11 T marked by a sharp increase in the resistances and a paramagnetic jump in the magnetization. As the field increases, the resistances show "fast oscillations" considerably larger than seen at temperatures above 5.5 K. More significantly, the magnetization, a thermodynamic measurement, shows oscillations. (This agrees with the recently reported behavior of the sound velocity [14], another thermodynamic measurement which shows oscillations at 5 but not at 6 K.) Comparing the 4 K with the 7.5 K results we infer that thermodynamic functions only exhibit the fast oscillations in an FISDW state and that we have crossed a barrier into such a state on cooling from 7.5 to 4 K above 11 T. Returning to the transport measurements at 4 K we note that, aside from the oscillations, the resistances first rise and then decrease with increasing field. The Hall resistance at high field is immeasurably small at the bottom of the oscillations, as in a metallic state [15]. At 2 K there is a transition at 8 T, and the resistances remain at high values to 23 T. Also interesting is the behavior of the magnetization, which here shows fast oscillations which are *inverted* from their behavior in the 4 K sweep. At 0.5 K one enters the extremely stable phase at 7.5 T and exits to a highly insulating phase with ill defined Hall resistance at 27 T as in previous reports [7].

In Fig. 4 we show the phase diagram constructed from many temperature and field sweeps on the properties measured above as well as ρ_{xx}, ρ_{yy}, and S_{xx}. The

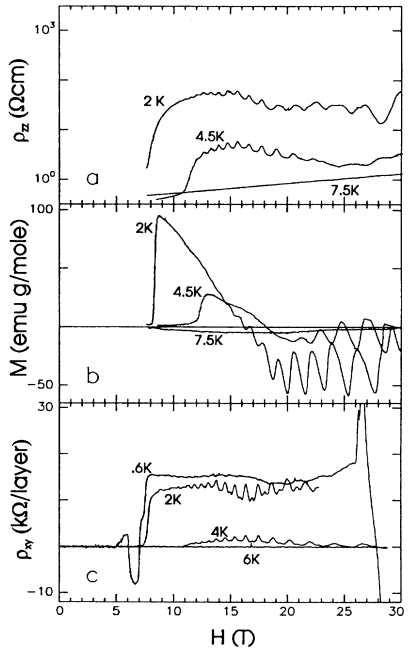

FIG. 3. Fixed temperature field sweeps of ρ_{zz}, ρ_{xy}, and magnetization. Note strong oscillations in data below 6 K, and the inversion of the oscillations in magnetization in going from 4 to 2 K. Also note the Hall resistance at 4 K first increases and then decreases to near zero as field is increased.

5.5 K transition is often difficult to detect with ρ_{xx} (it appears as a gradual increase). The higher temperature phase boundary is second order while the interior phase boundary is first order, as is seen from magnetization measurements (Fig. 2). Since there have been several predictions of an oscillating phase boundary for this material [10], special attention was placed on a search for these oscillations. The 5.5 K phase boundary shows no oscillations to better than 0.1 K. From each individual measurement it seems that there is a small phase boundary

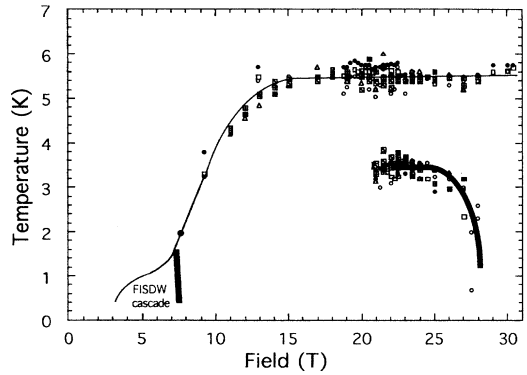

FIG. 4. Phase diagram arising from a compilation of measurements shown here and similar measurements on a number of additional samples. Thin lines are for second order transitions; heavy lines are for first order transitions.

oscillation at ~3.5 K, but comparison between, e.g., ρ_{zz} and magnetization shows no consistency. Any phase boundary oscillations are certainly less than 0.3 K and probably less than 0.1 K.

The present phase diagram differs from previous versions in the presence of two distinct transitions in the region from 23 to 27 T. In earlier publications it was thought that the 5.5 K transition gradually joined the 3.5 K transition in a continuous reentrant line. Figure 4 is the result of a much more extensive investigation, but particularly it is the result of the installation of a new set of field regulation coils in the hybrid II magnet at the Francis Bitter National Magnet Laboratory at MIT. This allowed considerably more measurement sensitivity and stability and more precise temperature control. Also note in Fig. 2 that at certain fields above 20 T magnetization and ρ_{xy} show virtually no indication of the 5.5 K transition. The thermopower measured transition at 3 K and 30 T [16] seems to coincide with present measurements at 5.5 K and 30 T.

How might such a remarkable phase boundary be possible? The observation of two distinct transitions in temperature sweeps in the field range 23–27 T suggests the possibility of separate transitions for the two pairs of Fermi surfaces at $\pm k_{F1}$ and $\pm k_{F2}$. At 6 K neither FS is gapped. At 5.5 K FS1 has a transition, and by 3.5 K there is a sizable gap and no conductance from FS1. But FS2 is metallic, and the total resistance is approximately doubled (as is seen). Moreover, between 5.5 and 3.5 K with FS2 metallic the Hall resistance remains small. Although FS1 and FS2 may have separate transitions, there are also interesting couplings between them. If the distortion wave vector is $2k_{F1}$ along **a** (i.e., the $n = 0$ insulating state for FS1), there will be small gaps induced by the magnetic periodicity ($\delta = ebH/hc$) on FS2 at $2k_{F1} + m\delta$. These gaps lie at $2k_{F2}$ when $2k_{F1} + m\delta = 2k_{F2}$ or $2k_{F2} - 2k_{F1} \approx 4t_b/\hbar v_F = m\delta$. Thus gaps appear at $2k_{F2}$ at the fast oscillation frequency. Another symmetry allowed coupling derives from Umklapp processes, since $2k_{F1} + 2k_{F2} = 2\pi/a$.

In terms of a Landau expansion we introduce $\Delta_{\alpha,n}$ as an order parameter for an FISDW on FSα with wave vector $q_\alpha = 2k_{F\alpha} + n\delta$. The periodicities then allow linear coupling between $\Delta_{1,n}$ and $\Delta_{2,m}$. (They also allow couplings between $\Delta_{1,n}$ and $\Delta_{2,\text{incom}}$ where the latter implies an order parameter on FS2 with wave vector $2k_{F1} + m\delta$, which, in general, is incommensurate with $2k_{F2}$.) These linear terms act as an effective field between $\Delta_{1,n}$ and the Δ_2's. These types of couplings can lead to induced gaps, coexisting order parameters on FS2, and first order transitions as well as soliton phases, commensurate lock-in, etc. [17].

To summarize our present thoughts, within the upper phase boundary $\Delta_{1,0}$ is finite and FS1 is insulating. Just inside the upper phase boundary $\Delta_{2,0}$ and $\Delta_{2,1}$ would be zero but they are induced finite by linear coupling to $\Delta_{1,0}$. At 26 T, 0.5 K $\Delta_{2,1}$ is large and dominates

$\Delta_{2,0}$. In traversing the first order phase line to arrive at 28 T, 0.5 K there is a discontinuous change to a state where $\Delta_{2,0}$ dominates $\Delta_{2,1}$. However, we can also go continuously between these two states by going around the critical point. In this case the high field state is the $n = 0$ insulator on both FS1 and FS2. On the other hand, the high field state might be dominated by one of the induced incommensurate phases $\Delta_{2,\text{incom}}$ instead of $\Delta_{2,0}$. This would explain why the state above the first order line appears metallic in Hall but shows a gradual crossover to insulating resistive behavior at low temperature. It would also explain why there are persistent fast oscillations to high field as the induced gaps sweep through ϵ_F or $4t_b/\delta$ = integer.

In conclusion, we present a new high field phase diagram for $(TMTSF)_2ClO_4$. It is constructed from data on one thermodynamic and five transport measurements from 11 different crystals. The results support several current ideas; the important role of the anion ordering, the coexistence of several order parameters, and interferences between the two pairs of Fermi surfaces. However, the essential ingredient that seems to have been missed was the possibility of distinct transitions on the two Fermi surfaces and the couplings that might result. These measurements still leave open to question whether the high field state is the long sought $n = 0$ insulator or a more subtle insulator resulting from localization in a superposition of incommensurate potentials in a quasi-one-dimensional interacting system.

We would like to acknowledge discussions with Dr. L. P. Gor'kov, Dr. A. G. Lebed, Dr. T. Halsey, Dr. K. Machida, and Dr. T. Osada, substantial conversations with Dr. S. Brazovskii, Dr. T. C. Lubensky, and Dr. V. Yakovenko, experimental assistance from Dr. S. Klepper and Dr. C. Immer and the hospitality of the Francis Bitter National Magnet Laboratory at MIT. This research was supported by NSF Grant No. DMR92-16155.

[1] For a review, see T. Ishiguro and K. Yamaji, *Organic Superconductors* (Springer-Verlag, Berlin, 1990), for more recent references, see G. Danner *et al.*, Physica (Amsterdam) **201B**, 442 (1994); in Proceedings of the ICSM94 [Synth. Met. (to be published)].

[2] L. P. Gor'kov and A. G. Lebed, J. Phys. Lett. **45**, L433 (1984); P. M. Chaikin, Phys. Rev. B **31**, 4770 (1985); G. Montambaux *et al.*, J. Phys. Lett. **45**, L-533 (1984); M. Heritier *et al.*, J. Phys. Lett. **45**, L-943 (1984); K. Yamaji, J. Phys. Soc. Jpn. **54**, 1034 (1985); M. Ya Azbel *et al.*, Phys. Lett. **117A**, 92 (1986); K. Maki, Phys. Rev. B **33**, 4826 (1986).

[3] S. T. Hannahs *et al.*, Phys. Rev. Lett. **63**, 1988 (1989); J. R. Cooper *et al.*, *ibid.* **63**, 1984 (1989).

[4] W. Kang *et al.*, Phys. Rev. Lett. **70**, 3091 (1993).

[5] M. Ribault, Mol. Cryst. Liq. Cryst. **119**, 91 (1985).

[6] M. J. Naughton *et al.*, Phys. Rev. Lett. **61**, 621 (1988).

[7] R. V. Chamberlin *et al.*, Phys. Rev. Lett. **60**, 1189 (1988).

[8] P. M. Chaikin *et al.*, Phys. Rev. Lett. **51**, 2333 (1983); H. Schwenk *et al.*, *ibid.* **56**, 667 (1986); T. Osada *et al.*, Solid State Commun. **60**, 441 (1986); Physica (Amsterdam) **143B**, 403 (1986); J. P. Ulmet *et al.*, *ibid.* **143B**, 400 (1986); X. Yan *et al.*, Phys. Rev. B **36**, 1799 (1987).

[9] K. Machida *et al.*, Phys. Rev. Lett. **70**, 61 (1993); K. Machida *et al.*, Phys. Rev. B **50**, 921 (1994).

[10] A. G. Lebed and P. Bak, Phys. Rev. B **40**, 11 433 (1989); K. Osada *et al.*, Phys. Rev. Lett. **69**, 1117 (1992).

[11] L. P. Gor'kov and A. G. Lebed, Phys. Rev. B **51**, 1362 (1995).

[12] Samples were cooled from 30 to 16 K over 36 h.

[13] There was not an independent absolute magnetization calibration on this run, so magnetization data are normalized to the jump observed at 0.8 K, 8 T in M. J. Naughton *et al.*, Phys. Rev. Lett. **55**, 969 (1985).

[14] X. D. Shi *et al.*, Phys. Rev. B **50**, 1984 (1994).

[15] The resistances show the same behavior as previously reported [6], but the previous interpretation was that the reentrance of the metallic phase was via as transition at the field where there is a substantial resistance drop (24 T). However, in light of the temperature sweeps reported above we rather suggest that the metallic reentrance is more of a gradual crossover than a transition at 4 K.

[16] R. C. Yu *et al.*, Phys. Rev. Lett. **65**, 2548 (1990).

[17] P. Barois, J. Prost, and T. C. Lubensky, J. Phys. **46**, 391 (1985).